5. TOXICITY AND BIOACCUMULATION

Factors 1 and 6 of the 10 factors for determining unreasonable degradation address concerns about the toxic and human health effects from discharges. This chapter provides a summary of the information available regarding the toxicity and the potential for bioaccumulation of water-based and synthetic-based drilling fluids.

5.1 Overview

The release of drilling and production wastes from oil and gas platforms is of interest due to the potential toxicity and the potential for bioaccumulation. The following is a brief summary of the available data regarding water-based and synthetic-based drilling fluids. It is important to note that the permit limits the toxicity of drilling fluids (30,000 ppm of the suspended particulate phase), prohibits the discharge of any muds containing diesel, the discharge of neat synthetic-based fluids, and limts the cadmium and mercury content of muds so that only the less contaminated sources of barite may be use in mud formulations. In addition, produced water discharges will not occur under this permit.

5.2 Toxicity of Drilling Fluids

Toxicity testing data are often used to assess the toxicologic characteristics of an effluent. Toxicity tests have been conducted with a wide variety of drilling muds, drilling mud fractions, and test organisms. The presence of diesel oil in used drilling mud also has been shown to contribute to increased toxicity (Conklin et al., 1983; Duke and Parrish, 1984).

The "fractions" or “phases” of drilling fluids that have been used in toxicity testing include:

Suspended Particulate Phase (SPP). One part by volume of drilling fluid is added to nine parts seawater. The drilling fluid-seawater slurry is well mixed and the suspension is allowed to settle for one hour before the supernatant SPP is decanted off. The SPP is mixed for five minutes and then used immediately in bioassays. Testing protocol currently employed by EPA specifies testing of the SPP.

Layered Solid Phase (LSP). A known volume of drilling fluid is layered over the bottom of the test vessel or added to seawater in the vessel. Although little or no mixing of the slurry occurs during the test, the water column contains a residual of very fine particulates which do not settle out of solution.

Suspended Solids Phase (SSP). Known volumes of drilling fluids are added to seawater and the mixture is kept in suspension by aeration or mechanical means.

Mud Aqueous Fraction (MAF). One part by volume of drilling fluid is added to either four or nine parts seawater. The mixture is stirred thoroughly and then allowed to settle for 20-24 hours. The resulting supernatant MAF is siphoned off for immediate use in bioassays. The MAF is

similar to the SPP but has a longer settling time, so the concentration of particulates in the supernatant is lower.

Filtered Mud Aqueous Fraction (FMAF). The mud aqueous fraction of whole drilling fluid is centrifuged and/or passed through a 0.45 μm filter and the resulting solution is the filtered mud aqueous fraction.

Because the synthetic-base fluids are water insoluble and the SBFs do not disperse in water as water-based drilling fluids (WBFs) do, but rather tend to sink to the bottom with little dispersion, most research has focused on determining toxicity in the sedimentary phase as opposed to the aqueous phase.

5.2.1 *Acute Toxicity*

Acute toxicity tests of whole drilling fluids have generally produced low toxicity. Petrazzuolo (1983) summarized the results of 415 such tests of 68 muds in 70 species and found 1 to 2 percent had LC50s ranging from 100 to 999 ppm, 6 percent had LC50s ranging from 1,000 to 9,999 ppm, 46 percent had LC50s ranging from 10,000 to 99,999 ppm, and 44 percent had LC50s of greater than 100,000 ppm (Table 5-1).

Test results also indicate that whole drilling fluid is more toxic than the aqueous or particulate fractions (Table 5-2). These data show whole fluid toxicity ranging from one to five times that of the aqueous fraction, and 1.3 times the toxicity of the particulate fraction. The reason for this increased toxicity is unclear, although a combination of chemical and physical interactions is possible. Also, in terms of using toxicity test results to project potential receiving water impacts, drilling fluids generally undergo a rapid physical separation of their solids components over once discharged.

Acute toxicity test results for used drilling fluids and drilling fluid components are presented in Appendix A. Criterion values for drilling fluid fractions in the table have been converted to whole fluid equivalents to provide greater comparability to whole fluid tests. For example, the MAF is prepared by mixing one part drilling mud with 9 parts seawater, so an LC50 value derived from 100 percent MAF is the supernatant from a 10 percent drilling fluid mixture and is therefore expressed as 100,000 ppm (10 percent whole fluid equivalent).

Petrazzuolo (1981) used a semi-quantitative procedure to rank organisms in terms of sensitivity to drilling fluids, based on laboratory tests. The results ranked groups of organisms as follows, in order of decreasing sensitivity: copepods and other plankton; shrimp; lobster; mysids and finfish; bivalves; crab; amphipods; echinoderms; gastropods and annelids; and isopods. This ranking is admittedly biased because it is limited by the actual bioassay test results that have been published, and not based on theoretical considerations. For example, if more tests, more toxic drilling fluids, and more sensitive life stages have been tested on certain types of organisms, they would appear to be more sensitive in the

rankings. These shortcomings notwithstanding, the ranking is a reasonable general indicator of the relative sensitivity of organisms to drilling fluids.

Table 5-1. Summary Table of the Acute Lethal Toxicity of Drilling Fluid[a]

	Number of species tested	Number of fluids tested	Number of tests	Not determinable	Number of 96-hr LC50 values (ppm)[b]				
					< 100	100-999	1,000-9,999	10,000-99,000	> 100,000
Phytoplankton	1	9	12	5	0	0	7	0	0
Invertebrates									
Copepods	1	9	11	1	0	3	5	2	0
Isopods	2	4	6	0	0	0	0	1	5
Amphipods	4	11	22	0	0	0	0	7	15
Gastropods	5	5	10	0	0	0	0	2	8
Decapods									
Shrimp	9	23	66	0	0	6(1)[c]	5	36	19
Crab	8	18	32	1	0	0	3	17	11
Lobster	1	2	7	0	0	0	1	3	3
Bivalves	11	22	59	19	0	0	1	19	20
Echinoderms	2	2	4	0	0	0	0	1	3
Mysids	4	17	64	2	0	0	1	29	32
Annelids	7	14	34	3	0	0	0	12	19
Finfish	15	24	80	0	0	0	2	50	36
TOTALS	70	40[d]	407	31	0	4-9	25	179	0.00

[a] Source: Adapted from Petrazzuolo, 1983.

[b] Placement in classes according to LC50 value. Lowest boundary of range if LC50 expressed as a range.
Cited values if given as ">" or "<." There were 199 such LC50 values; 95 were >100,000 ppm; 20 were <3,200 ppm.

[c] These include tests conducted on drilling fluids obtained from Mobile Bay, Alabama, and which may not be representative of drilling fluids used and discharged on the OCS. The value in parentheses is the result of not including those drilling fluids.

[d] The fluids used in Gerber et al., 1980, Neff et al., 1980, and Carr et al., 1980 were all supplied by API. Their characteristics were very similar and they may have been subsamples of the same fluids. If so, the total number of fluids tested would be 35.

Table 5-2. Comparison of Whole Fluid Toxicity and Aqueous and Particulate Fraction Toxicity for Some Organisms

Organism	Whole fluid vs. aqueous fraction	Whole fluid vs. particulate fraction
Gammarus (amphipod)	> 1.4 to 3.6:1	
Thais (gastropod)	> 1.2:1	
Crangon (shrimp)	> 1.1 to 1.4:1	
Carcinus (crab)	> 1.1 to 1.5:1	
Homarus (lobster)	> 3.5 to 5.3:1	
Strongylocentrotus (sea urchin)	> 2:1	
Coregonus (whitefish)	< 1.7:1	
Neomysis (shrimp)		1.3:1

Source: Petrazzuolo, 1981

Toxicity tests also highlight the toxicity variations that occur during a given organism's life cycle. Larval stage organisms are generally more sensitive than adult stages, and invertebrates are more sensitive while molting than during intermolt stages. These variations affect the potential for impact associated with offshore operations. Drilling fluids discharged into an area occupied by an adult community will presumably cause less impact than if the area were occupied by juvenile communities or if the area serves as a spawning ground.

Toxicity tests with larvae of the grass shrimp (*Palaemonetes intermedius*; Table 5-3) indicate that they are not as sensitive to whole muds as mysids. Average 96-hour LC50 values for whole muds ranged from 142 to 100,000 ppm. *Mercenaria mercenaria* one-hour-old larvae showed a lack of development (48-hour EC50) at relatively low concentrations of the liquid and suspended solids phases of the muds (Table 5-4). Concentrations as low as 87 and 64 ppm (respectively) halted larval development. Similarly, embryogenesis of *Fundulus* and echinoderms was affected by drilling fluid exposure. "Safe" levels (defined as a concentration of 10 percent of that having an adverse effect on the most sensitive assay system) ranged from one to 100 ppm. A study of sublethal effects of drilling mud on corals (*Acropora cervicornis*) indicated a decrease in the calcification rate and changes in amino acids at concentrations of 25 ppm.

All of the muds tested in an earlier used drilling mud study (Duke and Parrish, 1984) were found to contain some No. 2 fuel (diesel) oil. Surrogate "diesel" oil content ranged from 0.10 to 9.43 mg/g in the whole mud. Spearman rank order correlation of the relationship between toxicity and fuel oil content showed a significant correlation between these factors in all tests.

	Correlation Coefficient		
Test Material	Aromatic	Aliphatic	"Diesel"
Whole Mud	-0.79	-0.77	-0.81
Suspended Particulate Phase	-0.77	-0.89	-0.96

Table 5-3. Drilling Fluid Toxicity to Grass Shrimp (*Palaemonetes intermedius*) Larvae

Mud	Type	96-h LC50 (95% CI)	
MIB	Seawater Lignosulfonate	28,750 ppm	(26,332-31,274)
AN31	Seawater Lignosulfonate	2,390 ppm	(1,896-2,862)
SV76	Seawater Lignosulfonate	1,706 ppm	(1,519-1,922)
P1	Lightly Treated Lignosulfonate	142 ppm	(133-153)
P2	Freshwater Lignosulfonate	4,276 ppm	(2,916-6,085)
P3	Lime	658 ppm	(588-742)
P4	Freshwater Lignosulfonate	4,509 ppm	(4,032-5,022)
P5	Freshwater/Seawater	3,570 ppm	(3,272-3,854)
P6	Lignosulfonate	100,000 ppm	---
P7	Low Solids Nondispersed	35,420 ppm	(32,564-38,877)
P8	Lightly Treated Lignosulfonate	2,577 ppm	(2,231-2,794)
NBS Reference	Seawater/Potassium/Polymer	17,917 ppm	(15,816-20,322)

Source: Adapted from Duke and Parrish (1984). All tests conducted at 20 ppt salinity and 20+2°C with day-1 larvae.

Table 5-4. Results of Continuous Exposure (48 hr) of 1-hr Old Fertilized Eggs of Hard Clams (*Mercenaria mercenaria*) to Liquid and Suspended Particulate Phases of Various Drilling Fluids

Drilling Fluid	Liquid Phase EC50 (µl/l)[a]		Control % "D" Stage	Suspended Particulate EC50 (µl/l)[b]		Control % "D" Stage
AN31	2,427	(2,390-2,463)	88	1,771	(1,710-1,831)	93
MIB	>3,000		95	>3,000		95
SV76	85	(81-88)	88	117	(115-119)	93
P1	712		97	122	(89-151)	99
P2	318	(690-734)	97	156	(149-162)	99
P3	683	(308-328)	98	64	(32-96)	99
P4	334	(665-702)	98	347		99
P5	385	(324-345)	98	382	(330-364)	99
P6	>3,000	(371-399)	97	>3,000	(370-395)	93
P7	>3,000		97	2,799		93
P8	269		93	212	(2,667-2,899)	93
		(257-280)			(200-223)	

a EC50 and 95% confidence interval. The percentage of each test control (n = 625+125 eggs) that developed into normal straight-hinge or "D" stage larvae and the EC50 are provided.

Source: NEA, 1984.

Other studies also implicated diesel and mineral oil in the toxicity of certain drilling fluids. In these studies, the toxicity of drilling fluids with and without added diesel or mineral oil were compared (Table 5-5). The drilling fluids tested included "used" fluids as well as a National Bureau of Standards (NBS) reference fluid which contained no measurable amount of diesel. In each case, the addition of diesel or mineral oil increased the toxicity of the drilling fluids.

Conklin et al. (1983) also found a significant relationship between the toxicity of drilling fluids and diesel oil content. Their study was designed to assess the roles of chromium and petroleum hydrocarbons in the total toxicity of whole mud samples from Mobile Bay to adult grass shrimp (*Palaemonetes pugio*). The range of 96-hour LC50 values was from 360 to 14,560 ppm. The correlation between chromium concentration of the mud and the LC50 value was not significant; however, the correlation between diesel oil concentration and the LC50 value was significant. As the concentration of diesel oil in the muds increased, there was a general increase in the toxicity values. Similar toxicity tests using juvenile sheepshead minnows (*Cyprinodon variegatus*) showed higher LC50 levels but no significant correlation between either chromium or diesel oil content and toxicity.

Diesel oil appeared to be a key factor in drilling fluid toxicity. It may explain some of the increased toxicity of used versus unused drilling fluids. As a result of these data, EPA has prohibited the discharge of drilling fluids to which diesel oil has been added.

Table 5-5. Toxicity of API #2 Fuel Oil, Mineral Oil, and Oil-Contaminated Drilling Fluids to Grass Shrimp (*Palaemonetes intermedius*) Larvae

Materials Tested	Oil Added (g/l)	Total Oil Content (g/l)	96-hr LC50 (95% CI)[a] (ppm; µl/l)
API #2 fuel oil[b]	---	---	1.4 (1.3-1.6)
	---	---	11.1 (9.8-12.5)
Mineral Oil[c]	None	0.68	35,400 (32,564-8,877)
P7 mud	17.52	18.20	177 (165-190)
P7 mud + API #2 fuel	17.52	18.20	184 (108-218)
P7 mud + API #2 fuel oil (hot-rolled)	17.52	18.20	538 (446-638)
P7 mud + mineral oil	17.52	18.20	631 (580-674)
P7 mud + mineral oil (hot-rolled)	None	0	17,900 (15,816-20,332)
NBS reference drilling mud	18.20	18.20	114 (82-132)
NBS mud + API #2 fuel oil	18.20	18.20	116 (89-133)
NBS mud + API #2 fuel oil (hot-rolled)	18.20	18.20	778 (713-845)
NBS mud + mineral oil	18.20	18.20	715 (638-788)
NBS mud + mineral oil (hot-rolled)	None	18.20	142 (133-153)
P1 drilling mud			

a 95% confidence intervals computed by using a "t" value of 1.96.

b Properties: Specific gravity at 20°C, 0.86; pour point -23°C; viscosity, saybolt, 38°C, 36; saturates, wt% 62; aromatics, wt% 38; sulfur, wt%, 0.32.

c Properties: Specific gravity at 15.5°C, 0.84-0.87; flash point, 120-125°C; pour point, -12 to -15°C; aniline point, 76-78°C; viscosity, cst 40°C, 4.1 to 4.3; color saybolt, +28; aromatics, wt%, 16-20; sulfur, 400-600 ppm.

Source: Adapted from Duke and Parrish, 1984.

SBFs have routinely been tested using the Suspended particulate phase (SPP) toxicity test and found to have low toxicity (Candler et al., 1997). Rabke et al. (1998), have recently presented data from an interlaboratory variability study indicating that the SPP toxicity results are highly variable when applied to SBFs, with a coefficient of variation of 65.1 percent. Variability reportedly depended on such things as mixing times and the shape and size of the SPP preparation containers. As part of the coastal effluent guidelines effort, published in December 1996, EPA identified the problems with applying the SPP toxicity test to SBFs due to the insolubility of the SBFs in water (USEPA, 1996).

North Sea testing protocols require monitoring the toxicity of fluids using a marine algae (*Skeletonema costatum*), a marine copepod (*Arcartia tonsa*), and a sediment worker (*Corophium volutator* or *Abra alba*). The algae and copepod tests are performed in the aqueous phase, whereas the sediment worker test uses a sedimentary phase. Again, because the SBFs are hydrophobic and do not

disperse or dissolve in the aqueous phase, the algae and copepod tests are only considered appropriate for the water soluble fraction of the SBFs, while the sediment worker test is considered appropriate for the insoluble fraction of the SBFs (Vik et al., 1996). As with the aqueous phase algae and copepod tests, the SPP toxicity test mentioned above is only relevant to the water soluble fraction of the SBFs (Candler et al., 1997).

Both industry and EPA identified the need for more appropriate toxicity test methods for assessing the relative toxicities of various SBFs. Data presented by industry and EPA have shown that the abbreviated acute toxicity test of 96 hours increases the discriminatory power between the toxicity of individual SBFs and between the toxicity of SBFs and diesel (USEPA 2000). Both EPA and industry data have indicated that esters are the least toxic followed by internal olefin (IO), linearalphaolefin (LAO) and paraffins. These data also indicate toxicity for all base fluids tested and variability within individual tests both increase with increased test duration. Industry data indicate that a suitable 100%-formulated sediment for dilution sediment has yet to be developed. The toxicity data on SBFs and SBF base fluids are summarized in Table 5-6 and Table 5-7.

Table 5-6. Reported Toxicities of Synthetic-Based Fluids (LC50s)

	Ampelisca abdita	*Leptocheirus plumulosus*	*Rhepoxynius abronius*	*Corophium volutator*	*Abra alba*	*Skeletonema costatum*	*Acartia tonsa*	*Fundulus grandis*
BASE FLUID - Natural Sediment								
Diesel Candler, 1997 Rabke, 1998b Still, 1997	879 mg/kg 1.0 ml/kg 0.7 ml/kg	850 mg/kg	24 mg/kg	840 mg/kg				
EMO Candler, 1997 Still, 1997	557 mg/kg	251 mg/kg	239 mg/kg	7146 mg/kg				
IO Candler, 1997 Rabke, 1998b Vik, 1996 Still, 1997	3121 mg/kg 4.0 ml/kg 3.0 ml/kg	3.7 ml/kg 2,944 mg/kg	299 mg/kg	>30,000mg/kg 7,100 mg/l	300 mg/l	2,050 mg/l	>10,000 mg/l	

	Ampelisca abdita	*Leptocheirus plumulosus*	*Rhepoxynius abronius*	*Corophium volutator*	*Abra alba*	*Skeletonema costatum*	*Acartia tonsa*	*Fundulus grandis*
PAO Candler, 1997 Rabke, 1998b Vik, 1996 Still, 1997	10,690 mg/kg 13.4 ml/kg 12.5 ml/kg	9,636 mg/kg	975 mg/kg	>30,000mg/kg 12.0 ml/kg 3.0 ml/kg	7,900 mg/l	3,900 mg/l	>50,000 mg/l	
Ester Vik, 1996a					>100,000 mg/l	60,000 mg/l	50,000 mg/l	
Acetal Vik, 1996a					549 mg/l	>100,000 mg/l	>100,000 mg/l	
LAO Vik, 1996a					1,021 mg/l	>10,000 mg/l	>10,000 mg/l	
BASE FLUID - Formulated Sediment								
Diesel Rabke, 1998b		1.0 ml/kg 0.7 ml/kg						
WHOLE FLUID - Natural Sediment								
Diesel Rabke, 1998b	1.5 ml/kg	9.4 ml/kg						

	Ampelisca abdita	*Leptocheirus plumulosus*	*Rhepoxynius abronius*	*Corophium volutator*	*Abra alba*	*Skeletonema costatum*	*Acartia tonsa*	*Fundulus grandis*
IO Rabke, 1998b Friedheim et al., 1996	1.5 ml/kg	2.3 ml/kg		7,131 mg/kg	303 mg/kg			
PAO Rabke, 1998 Jones, 1991 Friedheim et al., 1996 Vik, 1996a	3.7 ml/kg	36.5 ml/kg		>10,000 mg/kg >10,000 mg/l	572 mg/kg 7,000 mg/l	82,400 mg/l	>50,000 mg/l	>8.4% TPH
Ester Vik, 1996a							34,000-145,000 mg/l	>50,000 mg/l
LAO Friedheim et al., 1996				1,268 mg/kg	277 mg/kg			
WHOLE FLUID - Formulated Sediment								
Diesel Rabke, 1998b		2.9 ml/kg 1.7 ml/kg 0.7 ml/kg 1.3 ml/kg						

	Ampelisca abdita	*Leptocheirus plumulosus*	*Rhepoxynius abronius*	*Corophium volutator*	*Abra alba*	*Skeletonema costatum*	*Acartia tonsa*	*Fundulus grandis*
IO								
Rabke, 1998b	3.6 ml/kg	2.5 ml/kg 2.7 ml/kg 10.5 ml/kg						
Hood, 1997		2,279 mg/kg 4,498 mg/kg 2,245 mg/kg 1,200 mg/kg 943 mg/kg						
PAO								
Rabke, 1998b		<2.5 ml/kg						
WHOLE FLUID -No Sediment								
	Mysidopsis bahia							
IO								
Rabke, 1998a	221,436 - >1,000,000 ppm (SPP)							
Hood, 1997	56,500 - >1,000,000 ppm (SSP)							

Table 5-7. Minimum and Maximum LC50 Values for New Sediment Toxicity Data Presented as Comment Response on Either the Proposed Rule (12/99) or the Notice of Data Availability (4/00) for Effluent Limitations Guidelines for the Oil and Gas Extraction Point Source Category.

	Minimum and Maximum LC 50 Values (mg/kg)				
	96-h LC 50			10-day LC 50	
Base Fluid	Minimum	Maximum		Minimum	Maximum
Diesel NS[a]	NA	NA		343[b,c]	NA
	776[b,d]			340[b,d]	
	892[e]	1133[e]		585[e]	951[e]
	703[b,f]			138[f]	635[f]
Diesel FS[g]	255[e]	374[e]		157[e]	312
	450[h]	703[h]		495[h]	495[h]
Ester NS	7686[d]	21824[d]		4275[d]	10,219[d]
	>12,800[b,e]			8743[b,e]	
Ester FS	27,986[b,e]			2816[b,e]	
IO NS	5874[c]	6306[c]		464[c]	2501[c]
	2675[d]	>8000[d]		2416[d]	2530[d]
	10,306[e]	19,522[e]		1988[e]	5270[e]
	27,269[f]	37,035[f]		2075[f]	16,131[f]
IO FS	<500[c]	2624[c]		<500[b,c]	
	3128[e]	17,501[e]		626[e]	1422[e]
	2289[h]	5913[h]		--	--
Paraffin NS	--	--		111[c]	1047[c]
	2263[b,d]			1151[b,d]	
	3241[b,f]			600[b,f]	1233[b,f]
LAO NS	--	--		205[c]	407[c]
	930[d]	2921[d]		1065[d]	1207[d]
PAO NS	2841[b,e]			707[b,e]	
PAO FS	2275[b,e]			333[b,e]	

[a] natural sediment

[b] one data point reported

[c] reported by Commenter III.B.b.9 Public Comments PR

[d] EPA unpublished data [e] Commenter A.a.13 NODA
[f] Commenter A.a.30 NODA
[g] Formulated Sediment [h] Commenter A.a.29 NODA

Summary

Since the original EA for the proposed SBF guidelines, both EPA and industry have conducted studies to evaluate the sediment toxicity of SBFs. Industry's initial attempt to examine different test organisms yielded a series of range-finder data that lead to the use of the amphipod *Leptocheirus plumulosus* as the primary test organism. Industry also examined the use of formulated sediments. Results of testing formulated sediments and estuarine organisms appeared to be more difficult than expected and industry, although continuing research on the issue, has suspended further testing with formulated sediments. Both EPA and industry's data have lead to the following assumptions on the toxicity of SBF.

- The ranking for the SBF toxicity from least toxic to most is esters-IOs-LAOs-PAOs-paraffins.

- Although formulated sediments appear to indicate more discriminatory power between individual base fluids, control mortality continues to be a problem with 100% formulated sediments.

- The abbreviated acute test of 96 hours increases discriminatory power between individual SBFs, however they are not to true measure of SBF toxicity.

- The toxicity of SBFs appear to increase with time (in comparison of a 96-hour exposure to a 10-day exposure).

5.2.2 *Chronic Toxicity*

Stress Tests on Corals

There has been considerable investigation regarding the effects of whole drilling fluids on corals, due to their sensitivity, ecological interest, and presence in the Texas Flower Garden Banks area. Respiration, excretion, mucous production, degree of polyp expansion, and clearing rates for materials deposited on the surface are all useful parameters for indicating stress.

Laboratory experiments using the corals *Montastrea* and *Diplora* showed essentially unchanged clearing rates after applications of calcium carbonate, barite, and bentonite. However, exposure to a used drilling fluid significantly decreased clearing rates, although dose quantification was not possible (Thompson and Bright, 1977). When seven coral species were studied using *in situ* exposures to used drilling fluid, *Montastrea* and *Agaricia* displayed no mortality after a 96-hour exposure to 316 ppm concentration, but 100 percent mortality at the 1,000 ppm level (Thompson and Bright, 1980). Stress reaction were displayed by six species at the 316-ppm exposure level, including partial or complete polyp retraction and mucous secretion. A similar response was observed after a 96-hour exposure to 100 ppm.

Thompson, in an undated report to the USGS, exposed *Montastrea* and *Porites* to used drilling fluids from a well of 4,200 m (13,725 ft) drilling depth. The corals were buried for eight hours under the fluid and then removed to a sand flat to observe recovery. The exposure produced tissue atrophy and decay, formation of loose strands of tissue, and expulsion of zooxanthellae (zooxanthellae are algae living within coral cells in a symbiotic relationship), all indicative of severe stress. The *Montastrea* colonies were dead 15 hours after removal, and the *Porites* colonies were dead after 10 days.

The effects of thin layer application to these species were also observed. *In situ* exposures of drilling mud produced no apparent effects on clearing rates; however, laboratory application did demonstrate effects. Applications of 10-mm thick carbonate sand or drilling fluid from a depth of either 4,200 m (13,800 ft) or 1,650 m (5,413 ft) were applied to the corals, with the following results:

- Colonies in the sand experiment cleared themselves in 4 hours
- Colonies in the 1,650-m fluid experiment cleared themselves in 2 hours
- Colonies in the 4,200-m fluid experiment were 20% (*Montastrea*) and 40% (*Porites*) cleared after 4 hours, 20% (*Montastrea*) and 100% (*Porites*) cleared after 26 hours.

Additional testing with *Porites* indicated that the 4,200-m fluid was more toxic than the 1,650-m fluid, probably because the use of additives increases with well depth. No data are available on actual drilling fluid composition, however.

Krone and Biggs (1980) exposed coral (*Madracis decactis*) to suspensions of 100-ppm drilling mud from Mobile Bay, Alabama, which had been spiked with 0, 3, and 10 ppm ferrochrome lignosulfonate (FCLS). The drilling mud was presumably one with a low (<1 ppm) FCLS concentration. The corals were exposed for 17 days, at which time they were placed in uncontaminated seawater and allowed to recover for 48 hours. All of the corals exposed to the FCLS-spiked mud exhibited short-term increases in oxygen consumption and ammonia excretion. Photographic documentation of the corals revealed a progressive development of the following conditions: 1) a reduction in the number of polyps expanded indicating little or no active feeding; 2) extrusion of zooxanthellae; 3) bacterial infections with subsequent algal overgrowth; and 4) large-scale polyp mortality in two of the colonies. Coral behavior and condition improved dramatically during the recovery period. Polyps of surviving corals reexpanded and fed actively on day two of the recovery period.

Dodge (1982) evaluated the effects of drilling fluid exposure on the skeletal extension of reef-building corals (*Montastrea annularis*). Corals were exposed to 0, 1, 10, or 100 ppm drilling fluid ("Jay" fluid) for 48 days in a flow-through bioassay procedure. The drilling mud composition was changed approximately weekly as new mud taken from the well was added. One significant change in mud composition was in the diesel oil content, which was 0.4% by weight from the fourth week to the end of the experiment. Corals exposed to 100 ppm had significantly depressed linear growth rates and increased mortality. Calcification rates of corals exposed to 100 ppm decreased by 53% after four weeks and by

84% after six weeks. There was no indication of lowered growth rates for either the 1- or 10-ppm exposure.

Hudson and Robbin (1980) exposed corals (*Montastrea annularis*) to unused drilling fluid in heavy doses of 2- to 4-mm layers applied four times at 150-minute intervals. Drilling mud particles were generally removed by a combination of wave action, tentacle cleansing action, and mucous secretions. At the end of the exposure period, corals were placed in protected waters for six months. At the end of another six months, the corals were removed and examined for growth characteristics. Results of the growth analysis indicated that heavy concentrations of drilling mud applied directly to the coral surface over a period of only 7½ hours reduced growth rates and suppressed variability. Trace element analyses of the corals indicated that neither barium nor chromium incorporated into the skeletal materials.

Experiments with the coral *Acropora cervicornis* revealed reduced calcification rates after exposure to concentrations as low as 25 ppm of used Mobile Bay drilling mud (Kendall et al., 1983). Calcification rates in growing tips were reduced to 88%, 83%, and 62% of control values after 24-hour exposures to 25, 50, and 100 ppm (v/v) drilling mud, respectively. Effects on soluble tissue protein and ninhydrin positive substance were also noted at these or higher levels. Further experiments with kaolin, designed to reproduce the turbidity levels of the drilling mud without its chemical effects, revealed slight metabolic changes to the corals that were much less pronounced than those observed for the drilling mud treatments.

5.2.3 *Long Term Sublethal Effects*

Crawford and Gates (1981) examined the effect of a Mobile Bay drilling mud (mud XVI) on the fertilization and development of the sand dollar *Echinarachnius parma*. Fertilization studies showed that sperm were highly refractive to the toxic action of this drilling mud. Exposure even at 10,000 mg solids/ml (a 26-fold dispersion of the whole mud) reduced fertilization by only 7 percent. Eggs were more sensitive; exposure to 1,000 mg/ml (262-fold dilution of the whole fluid) reduced fertilization from 88-90 percent to 4-6 percent. No effect was noted at 100 mg/ml (2,620-fold whole mud dilution). At this same exposure level (100 mg solids/ml), no effects were observed in development. At 1,000 to 10,000 mg solids/ml, development was delayed.

No EC50/LC50 ratio could be determined from these data. However, the apparent lower limit of 1,000 ppm drilling mud as the lowest level that results in statistically significant sublethal reproductive changes is consistent with other data. For example, killifish (*Fundulus heteroclitus*) embryos were exposed to a seawater-lignosulfonate mud (Neff et al., 1980). Several parameters were examined, including percentage hatch, percentage increased time to hatch, percentage decreased heart rate, and anomalies at day 16. Although no EC50/LC50 ratios could be calculated, data were available to plot and obtain EC01 values. These ranged from 1,000 to 6,000 ppm. For the shrimp *Palaemonetes pugio*, exposure to 1,000 to 10,000 ppm of a high density lignosulfonate mud did not alter the duration of any larval instar (Neff et al., 1980).

The effects of 6-week exposures to the aqueous phases of both medium- and high-density lignosulfonate muds on the condition index (dry meat weight/shell weight) of oyster spat (*Crassostrea gigas*) have been reported (Neff et al., 1980). For the medium-density mud (12.6 lb/gal), no effect was noted at 5,000 ppm or 10,000 ppm whole mud equivalents. The index was reduced about 20 percent at 20,000 ppm. For the high-density mud (17.4 lb/gal), approximately a 30 percent reduction occurred in the index at all concentrations tested.

Mussels (*Mytilus* sp.) were exposed to 50 ppm TSS for 30 days by Gerber et al. (1980). Growth was 75 percent of that observed in control animals. It is not known, however, whether this represents a process of reversible growth retardation or irreversible growth inhibition.

Juvenile mysids were exposed to 15,000-75,000 ppm of the aqueous phase of a lignosulfonate mud for 7 days by Carr et al. (1980). On a dry-weight basis, no effect on respiration occurred. This contrasts with the increased respiration seen in shrimp exposed to 35,000 ppm of the same mud's aqueous phase and suggests that compensatory adaptation had occurred. Average dry weights were significantly lower in exposed shrimp.

When polychaetes (*Nereis* sp.) were exposed to 100,000 ppm of the aqueous phase of a lignosulfonate mud for 4 days, glucose-6-phosphate dehydrogenase activity was significantly decreased (Gerber et al., 1980). Activity recovered, however, during a 4-day depuration period.

Histologic alterations were noted following exposure of grass shrimp to 100 ppm or 500 ppm barite for 30 days (Conklin et al., 1980). Mortalities in two replicates of the experiment were 20 percent for control shrimp and 60 percent for exposed shrimp (no concentrations of barite given). In 40 percent of the surviving shrimp, there were no histologic changes. In the remainder of surviving shrimp, a variety of changes were noted, including: absence of posterior midgut epithelia (20 percent of the survivors); degenerative changes in microvilli; dilated and hypertrophied rough endoplasmic reticulum; and both nuclear and Golgi changes. Barite was also observed in statocysts. Although controls were provided with a sand substrate, exposed shrimp were not. Thus, it remains unclear whether such changes would occur in a sediment-barite mixture. Also, because of concerns over settling of barite particles, no dose-response relationship could be identified or constructed from the data.

Lobsters were exposed to a Jay field fluid (an onshore operation) for 36 days in a flow-through system by Atema et al. (1982). The exposure was nominal at 10 mg/l. However, settling of solids was noted and the actual exposure was undefined. The number of dead or damaged lobsters was not significantly different from controls. The number of dead plus damaged lobsters was significantly higher among treated animals. Although molts from larval stage IV to V were unaffected, molts from stage V to VI were delayed in exposed animals. Exposed lobsters also exhibited poor coordination and food alert suppression.

Three studies in a Gulf of Mexico laboratory examined the effects of drilling muds or drilling mud components on community recruitment and development of benthic macrofauna (Tagatz et al., 1980; Tagatz and Tobia, 1978) and meiofauna (Cantelmo et al., 1979). Test substances were mixed at various ratios with sediment, or were applied as a covering layer over sediment in a flow-through system.

The tests conducted with drilling mud indicated that annelids were the most sensitive group, exhibiting significant reductions in abundance at 1:10 and 1:5 mixtures of mud and sediment, as well as when exposed to a covering of drilling mud (Tagatz et al., 1980). This sensitivity of annelids was also observed for a similar experiment conducted with barite as the toxicant. Coelenterate abundance was also significantly reduced by exposure to the 1:5 mixture of mud and sediment and the drilling mud covering. Arthropods were affected only by a drilling mud covering. Mollusks were not significantly affected by exposure to drilling mud, but were reduced in abundance when exposed to barite covering (Tagatz and Tobia, 1978). Annelid abundance was also reduced by exposure to barite covering (Tagatz and Tobia, 1978), but no other groups were significantly affected. Exposure to barite as a mixture in sediment significantly increased the abundance of nematodes and increased total meiofaunal density, whereas barite layering slightly reduced total meiofauna density and densities of nematodes and copepods. The reduction was not statistically significant (Cantelmo et al., 1979).

Certain difficulties arise in the interpretation of these data. First, results for total abundance are apparently skewed by the greater sensitivity of a certain few predominant species. This does not affect the significance of the results within the constraints of this experiment, but may reduce the applicability of these results to areas *in situ* where community structure is not similar to those observed in this experiment. Second, any attempt to relate these studies to effects *in situ* is confounded by the absence of sediment barium levels given for these studies. Barium is the only useful tracer of drilling mud dispersion in the sediment.

5.2.4 *Metals*

The potential accumulation of metals in biota represents an issue of concern in the assessment of oil and gas impacts. Sublethal effects resulting from bioaccumulation of these highly persistent compounds are most often measured. Gross metal contamination from drilling fluids may also cause mortality, particularly in benthic species. Sources of metals include drilling fluids, produced waters, sacrificial anodes, and contamination from other minor sources. Drilling fluids and produced waters are the primary sources of the metals of concern: arsenic, barium, chromium, cadmium, copper, mercury, nickel, lead, vanadium, silver, and zinc.

Field studies of metal concentration in sediments around platforms suggest that enrichment of certain metals may occur in surface sediments around platforms (Tillery and Thomas, 1980; Mariani et al., 1980; Crippen et al., 1980; and others). In the review of these studies conducted by Petrazzuolo (1983), enrichment of metals around platforms is generally distance dependent with maximum enrichment factors seldom exceeding ten. In platforms studied, enrichment of metals that could be

attributed to drilling activities was either generally distributed to 300-500 m around the platform, or distributed downcurrent in a plume to a larger distance from the structure.

The concentrations of metals required to produce physiological or behavioral changes in organisms vary widely and are determined by factors such as the physicochemical characteristics of the water and sediments, the bioavailability of the metal, the organism's size, physiological characteristics, and feeding adaptations. Metals are accumulated at different rates and to different concentrations depending on the tissue or organ involved. Laboratory studies on metal accumulation as a result of exposure to drilling muds have been conducted by Tornberg et al. (1980), Brannon and Rao (1979), Page et al. (1980), McCulloch et al. (1980), Liss et al. (1980), and others. Data from these laboratory studies are summarized in Appendix B. Maximum enrichment factors for the metals measured were generally low (<10) with the exception of barium and chromium, which had enrichment factors of up to 300 and 36, respectively.

Depuration studies conducted by Brannon and Rao (1979), McCulloch et al. (1980), and Liss et al. (1980) have shown that organisms tested have the ability to depurate some metals when removed from a zone of contamination. In various tests, animals were exposed to drilling fluids from 4-28 days, followed by a 1-14 day depuration period. Uptake and depuration of barium, chromium, lead, and strontium were monitored and showed a 40-90% decrease in excess metal in tissues following the depuration period. Longer exposure generally meant a slower rate of loss of the metal. In addition, if uptake was through food organisms rather than a solute, release of the excess metal was slowed.

The available laboratory data on metals accumulation are difficult to correlate with field exposure and accumulation. Petrazzuolo's review (1983) notes that in the field, bioaccumulation of metals in the benthos will result from exposure to the particulate components of drilling muds. However, laboratory studies have almost always used either whole fluids or mud aqueous fractions, and thus are either over- or underestimating potential accumulation.

Field studies of metal accumulation in marine food webs off southern California have been conducted by Schafer et al. (1982) and others. These data have indicated that most metals measured (including Cr, Cu, Cd, Ag, Zn) do not increase with trophic level either in open water or in contaminated regions such as coastal sewage outfalls.

5.3 Bioaccumulation Potential of Synthetic-Based Drilling Fluids

One factor considered in assessing the potential environmental impacts of discharged drilling fluids and drill cuttings is their potential for bioaccumulation. This section presents information concerning the bioaccumulation of oleaginous-base fluids, including the synthetic-base fluids and mineral oil.

Most of the available information has been developed by mud suppliers to provide information to government regulators to assess the acceptability of these materials for discharge into the marine environment. The available information on the bioaccumulation potential of synthetic base fluids is scant, comprising only a few studies on octanol:water partition coefficients (P_{ow}) and three on tissue uptake in experimental exposures. The P_{ow} represents the ratio of a material that dissolves or disperses in octanol (the oil phase) versus water. The P_{ow} generally increases as a molecule becomes less polar (more hydrocarbon-like). EPA reviewed the available information on the bioaccumulation potential of synthetic-base fluids (USEPA, 2000). The review covers four types of synthetics: an ester (two studies), internal olefins (IO; four studies), and poly alpha olefins (PAO; five studies). One study included a low toxicity mineral oil (LTMO) for comparative purposes. The types of synthetic-base fluids tested represent the more common of synthetic-base fluid types currently in use in drilling operations.

The data that EPA identified concerning the bioaccumulation potential of synthetic base fluids are summarized in Table 5-8. Nine reports provided original information. This information consisted of P_{ow} data (based on calculated or experimental data), dispersibility data, or subchronic exposure of test organisms to yield data for calculating BCFs or assessing uptake. log P_{ow} values less than three or greater than seven would indicate that a test material is not likely to bioaccumulate (Zevallos et al., 1996).

For PAOs, the log P_{ow}s reported were >10, 11.19, 11.9, 14.9, 15.4, and 15.7 in the five studies reviewed. The four studies of IOs that were reviewed reported log P_{ow}s of 8.57 (8.6) and >9. The ester was reported to have a log P_{ow} of 1.69 in the two reports in which it was presented. The LAO log P_{ow} was cited as 7.82 and a log P_{ow} of 15.4 was reported for an LTMO. The only BCF reported was calculated for

Table 5-8. Bioaccumulation Data for Synthetic Fluids and Mineral Oil Muds

Type of Synthetic Base Fluid or LTMO	Parameter Determined	Reference
PAO	log P_{ow}: 15.4 (calculated)	Friedheim et al., 1991
PAO	log P_{ow}: >10 (calculated)	Leutermann, 1991
PAO	log P_{ow}: 14.9 - 15.7 (measured)	Schaanning, 1995
PAO	log P_{ow}: 11.9 (measured)	Zevallos et al., 1996
PAO	log P_{ow}: 11.19	Moran, 2000
IO	log P_{ow}: > 9	Environment & Resource Technology, Ltd., 1994a
IO	log P_{ow}: 8.57	Zevallos et al., 1996; Moran, 2000
LAO	log P_{ow}: 7.82	Moran, 2000
Ester	log P_{ow}: 1.69	Growcock et al., 1994; Moran, 2000
LTMO	log P_{ow}: 15.4	Growcock et al., 1994
various	dispersibility: ranking = ester> di-ether >> detergent alkylate > PAO > LTMO	Growcock et al., 1994
IO	10-day uptake; 20-day depuration exposure gave log BCF: 5.37 (C16 forms); 5.38 (C18 forms)	Environment & Resource Technology, Ltd., 1994b; Moran, 2000
PAO	Uptake: no measured uptake in tissues after 30-day exposure; presence noted in 1 of 24 gut samples	Rushing et al., 1991; Moran, 2000
LTMO	Uptake: after 30-day exposure, detectable amounts in 50% of tissues analyzed (12 of 24) and 19 of 24 gut samples examined	Rushing et al., 1991
PAO	Subchronic effects: equal or better growth vs controls	Jones et al., 1991
LTMO	Subchronic effects: retarded growth vs controls	Jones et al., 1991
LAO	Mytilus edulis log BCF: 4.84	Moran, 2000

Abbreviations: PAO: poly alpha olefin; IO: internal olefin; LAO: linear alpha olefin; LTMO: low toxicity mineral oil

IOs; a value of 5.4 l/kg was determined. In 30-day exposures of mud minnows (*Fundulus grandis*) to water equilibrated with a PAO- or LTMO-coated cuttings, only the LTMO was reported to produce adverse effects and tissue uptake/occurrence. Growth retardation was observed for the LTMO and LTMO was observed at detectable levels in 50% of the muscle tissue samples examined (12 of 24) and most (19 of 24) of the gut samples examined. The PAO was not found at detectable levels in any of the muscle tissue samples and occurred in only one of twenty-four gut samples examined.

These limited data suggest that synthetic base fluids do not pose a serious bioaccumulation potential. Despite this general conclusion, existing data cannot be considered sufficiently extensive to be conclusive. This caution is specifically appropriate given the wide variety of chemical characteristics resulting from marketing different formulations of synthetic fluids (i.e., carbon chain length or degree of unsaturation within a fluid type, or mixtures of different fluid types).